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(54) **Use of solutions of polyisocyanates and oligourethanes containing hydroxyl groups as adhesives for film composites**

(57) The use of solutions in organic solvents, inert relative to isocyanate groups, of a) organic polyisocyanates, b) oligourethanes containing hydroxyl groups, and optionally c) auxiliaries and additives as adhesives in the production of film composites, in which oligourethanes, optionally containing incorporated chain extenders and representing essentially urethane-modified ether group-free polyester polyols with a hydroxyl group content from 0.4 to 2.2 % by weight and a urethane group content from 1.4 to 7 % by weight, which contain both aliphatic and aromatic dicarboxylic acid segments in a form incorporated via ester groups, are used as component b).

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Use of solutions of polyisocyanates and oligourethanes containing hydroxyl groups as adhesives for film composites

The invention relates to the use of selected solvent-containing, two-component adhesives based on organic polyisocyanates and selected oligourethanes containing hydroxyl groups as adhesives in the production of film composites.

Film composites, for example, composites of polyethylene. polypropylene, polyamide, polyethylene terephthalate, cellophane or aluminum foils, with themselves or with each other are preferably produced using polyurethane adhesives. These adhesives are generally two-component adhesives based on linear polyurethanes and higher functional polyisocyanates as crosslinking agents, which are processed in the form of 10 to 40 % by weight solutions in low-boiling solvents. like ethyl acetate or acetone (cf. DE-OS 25 49 227).

There is a significant desire for low-solvent systems that can be processed on available lamination machines for ecological and economic reasons. However, this requires adhesives that have a solution viscosity of 150 mPa.s at most with a solids content of at least 45 % by weight. It is possible to produce two-component systems with the required low viscosity at high solids content of the solutions with the expedients known to polyurethane chemists, for example, by co-employment of reactive diluents or by using a significant diisocyanate excess in the production of the polyurethanes containing hydroxyl groups, but composites produced with such systems only have extremely low initial strength, which enormously hampers handling of the freshly prepared composites. Practice is also interested in adhesives that have the least possible solvent retention, so that removal of the solvent before production of the composites is possible by brief heating of the film coated with the adhesive.

The underlying task of the invention therefore was to furnish new two-component adhesives that meet the mentioned requirements of practice.

This task was solved by the use according to the invention of combinations of organic polyisocyanates with specific oligourethanes containing hydroxyl groups.

The use of combinations of organic polyisocyanates and oligourethanes containing hydroxyl groups as two-component film adhesives is already known, in principle, from DE-PS 2 318 440, but the adhesives described in this prior publication, based on urethane-modified polyether-polyester glycols, are also beset with the drawback of an unduly high viscosity for practical conditions.

The object of the invention is the use of solutions with a solids content of at least 45 % by weight in organic solvents inert relative to isocyanate groups of

a) at least one organic polyisocyanate with an (average) NCO functionality of at least 2.0,

b) at least one oligourethane containing hydroxyl groups with a molecular weight of 1500 to 8000, and

c) optionally the auxiliaries and additives known from adhesive technology,

in which the amounts of components a) and b) correspond to an NCO/OH-equivalent ratio of at least 1 : 1.5. as adhesives in the production of film composites, characterized by the fact that oligourethanes, optionally containing incorporated chain extenders, representing essentially urethane-modified ether group-free polyester polyols with a hydroxyl group content from 0.4 to 2.2 % by weight and a urethane group content from 1.4 to 7 % by weight, which contain both aliphatic, and also aromatic dicarboxylic acid segments in a form incorporated via ester groups, are used as component b).

Polyisocyanates or polyisocyanate mixtures with an average functionality of at least 2.0, preferably 2.3 to 3.5, are used as polyisocyanate component a). These are known polyisocyanates, like the product of the conversion of trimethylolpropane with toluene-2,4-diisocyanate (produced by conversion of a high excess of diisocyanate with triol with subsequent elimination of the unreacted diisocyanate excess by distillation), tris(isocyanatohexyl)biuret or its mixtures with higher homologues, polyisocyanates containing isocyanurate groups based on toluene-2,4-diisocyanate or polyisocyanate mixtures of the diphenylmethane series with the mentioned NCO functionality, as are accessible by means of the phosgenation of aniline-formaldehyde condensates in known fashion. Mixtures of diphenylmethane-2,4'- and -4,4'-diisocyanate, liquid at room temperature, are also suitable.

Oligourethanes with an average molecular weight of 1500 to 8000, preferably 3000 to 6000, which can be calculated from the stoichiometry of the starting materials, and having hydroxyl groups, are used as component b) in the adhesives to be employed according to the invention, containing from 0.4 to 2.2, preferably 0.6 to 1.4 % by weight hydroxyl groups and from 1.4 to 7 % by weight incorporated urethane groups -NH-CO-O-. These oligourethanes are urethane-modified polyester polyols, free of ether groups, optionally containing an incorporated chain extender, based on b_1) organic diisocyanates, b_2) ether group-free polyester polyols, and optionally b_3) low-molecular chain extenders.

Appropriate diisocyanates as constituent b_1) are those of the formula

$$Q(NCO)_2$$

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for which

Q stands for an aliphatic hydrocarbon group with 2 to 18, preferably 6 to 10 carbon atoms, a cycloaliphatic hydrocarbon group with 4 to 15, preferably 5 to 13 carbon atoms, an aromatic hydrocarbon group with 6 to 15, preferably 6 to 13 carbon atoms, or an araliphatic hydrocarbon group with 8 to 15, preferably 8 to 13 carbon atoms.

Typical examples of such diisocyanates are hexane-1,6-diisocyanate, decane-1,10-diisocyanate, cyclopentane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane, dicylcohexylmethane-4,4'-diisocyanate, benzene-1,4-diisocyanate, toluene-2,4-diisocyanate, its mixtures with up to 35 % by weight, in reference to the total mixture, of toluene-2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, its mixtures of up to 60 % by weight, in reference to the total mixture, of diphenylmethane-2,4'-diisocyanate, and optionally subordinate amounts of diphenylmethane-2,2'-diisocyanate or 1,4-bis(isocyanatemethyl)benzene. Particularly preferred constituents b_1) are toluene-2,4-diisocyanate, its mixtures of up to 35 % by weight, in reference to the total mixture, of toluene-2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, its mixtures with up to 60 % by weight, in reference to the total mixture, of diphenylmethane-2,4'-diisocyanate, which can contain subordinate amounts of diphenyl-methane-2,2'-diisocyanate (up to 5 % by weight), hexane-1,6-diisocyanate, dicyclohexyl-methane-4,4'-diisocyanate and 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate). However, any other organic diisocyanates, in principle, can also be used, like alkyl-substituted diphenylmethane diisocyanates, carbodiimide- or urethane-modified diphenylmethane-4,4'-diisocyanate or any mixtures of such diisocyanates. In principle, any mixtures of the aforementioned diisocyanates can be used, although this is less preferred.

The constituent b_2) is essentially a polyester diol, free of ether groups, with an average molecular weight from 1000 to 3000, preferably 1400 to 2500, which can be calculated from the hydroxyl number. However, it is essential that the polyester component b_2) contain both incorporated aliphatic and incorporated aromatic dicarboxylic acid segments in a molar ratio of aliphatic to aromatic dicarboxylic acids of 8 : 1 to 1 : 5, preferably 3 : 1 to 1 : 2, in which the use of mixtures of different polyester diols, whose individual components contain at least one dicarboxylic acid of the mentioned type, and also the use of only one polyester diol, containing both types of incorporated acids are considered. Starting materials for the production of polyester diols are organic dicarboxylic acids or their anhydrides and alkanediols with 2 to 6 carbon atoms.

Appropriate dicarboxylic acids include succinic acid, adipic acid, suberic acid, orthophthalic acid and isophthalic acid.

Appropriate alkanediols are those with a linear or branched carbon chain, like ethylene glycol, 1,2-dihydroxypropane, 1,3-dihydroxypropane, 1,4-dihydroxybutane, 1,6-dihydroxyhexane or neopentyl glycol.

As optionally used chain extender b_3), in addition to the diols just mentioned as structural components for the polyester diols, any di- and/or trihydric alcohols in the molecular weight range from 62 to 400 are considered, like 1,2-dihydroxypropane, 1,8-dihydroxyoctane, 1,4-bis(hydroxymethyl)cyclohexane, 2-methyl-1,3-dihydroxypropane, dimethylolpropionic acid, glycerol, trimethylolpropane, 1,2,6-trihydroxyhexane, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol. tripropylene glycol, dibutylene glycol or any mixtures of such polyhydric alcohols. These chain extenders are used, if at all, in amounts of up to 100 mol%, in reference to component b_2).

Production of the oligourethanes occurs according to known methods of the prior art by means of the reaction of the starting components in solution or preferably in a melt at 80 to 140°C, with maintenance of an NC/OH-equivalent ratio, in reference to the staring components, from 1 : 1.4 to 1 : 5.0, preferably 1 : 1.8 to 1 : 3.0.

If solvents are used in the production of oligourethane, solvents of the adhesives of the present type to be used according to the invention are preferably also used. These are inert solvents relative to isocyanate groups, like acetone, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate or any mixtures of such solvents, which can also contain aromatic diluents, like toluene or xylene.

It is particularly preferred, within the context of the invention. to use oligourethanes b), whose constituent b_2) consists essentially of a polyester mixture. The use of a polyester mixture from

(i) 50 to 90 % by weight of a polyester-diol with a molecular weight of 1400 to 3000 from adipic acid and o-phthalic acid in a molar ratio of 40 : 60 to 80 : 20 and alkanediols of the mentioned type

and

(ii) 10 to 50 % by weight of a polyester-diol with a molecular weight of 1000 to 3000 from adipic acid and a mixture of at least two alkanediols of the mentioned type, in which at least two of the alkanediols are present in an amount of at least 20 mol%,

has turned out to particularly advantageous. In the production of these oligourethanes, up to 100 mol%, in reference to the amount of polyester mixture, of chain extenders of the mentioned type can be co-employed.

The use of oligourethanes of the mentioned type, based on

b_1) toluene-2,4-diisocyanate or its mixtures with up to 35 % by weight, in reference to the total mixture, of toluene-2,6-diisocyanate

and

b_2) a polyester mixture from

(i) 70 to 85 % by weight of a polyester-diol with a molecular weight range of 1500 to 2500 from adipic acid and o-phthalic acid in a molar ratio of 40 : 60 to 70 : 30 and ethylene glycol

and

(ii) 15 to 30 % by weight of a polyester-diol with a molecular weight of 1500 to 2500 from adipic acid and a mixture of ethylene glycol and 1,4-dihydroxybutane in a molar ratio of 80 : 20 to 20 : 80,

in amounts corresponding to an equivalent ratio of isocyanate groups to hydroxyl groups from 1 : 1.8 to 1 : 3.0, is particularly preferred.

The auxiliaries and additives known from adhesive technology can be present in the adhesives to be used according to the invention as additional ingredients c). These are especially catalysts that accelerate the isocyanate addition reaction, like dibutyltin oxide, dibutyltin dilaurate, N,N-dimethylaniline, and/or triethylenediamine, UV stabilizers and/or tackifying resins. Co-employment of the last two mentioned additives, however, is less preferred.

The adhesives to be used according to the invention represent solutions of components a), b) and optionally c) in solvents inert relative to isocyanate groups of the aforementioned type. The amount of component a) in these solutions can be varied over wide limits. It is guided according to the amount of active hydrogen atoms of component a) and the type of film composite being produced. Generally. the amount of component a) corresponds to at least an NCO/OH-equivalent ratio, in reference to components a) and b), of at least 1 : 1.5. The amount of component a) preferably corresponds to an NCO/OH-equivalent ratio from 1 : 1.3 to 1 : 0.5.

The adhesives to be used according to the invention preferably represent solutions with a solids content, in reference to components a) to c), of 45 to 70 % by weight. The freshly prepared solutions, despite this high solids content, generally have a viscosity below 150 mPa.s. Preparation of the adhesive solution preferably occurs by combining the previously dissolved components a) and b), in which the solution of component b) also contains the component c) to be optionally employed. Processability of the solution so prepared at room temperature lasts for a period of about 8 hours.

The adhesive solutions to be used according to the invention are suitable for the production of film composites, i.e., composites of a wide variety of plastic films or metal foils with themselves or each other. Examples of films to be glued according to the invention can be gathered from the following practical examples.

Production of the film composites occurs in known fashion, for example, by coating at least one of the film surfaces to be joined together with the adhesive solution to be used according to the invention in an amount of about 0.5 to 10, preferably 1 to 5 g/m^2, in reference to solids. After

brief heating of the coated film to a temperature in the temperature range from 60 to 100°C for evaporation of most of the solvent, the film surfaces are joined.

The following examples serve to further explain the invention.

Examples

The following polyester-diols are used in the following examples:

I Mixed ester of adipic acid and o-phthalic acid (molar ratio 1 : 1) and ethylene glycol, OH number: 65; acid number: 1.3

II Mixed ester of adipic acid and ethylene glycol, 1,4-dihydroxybutane in a molar ratio 7 : 3. OH number 65; acid number: 1.0

III Mixed ester of adipic acid and ethylene glycol. 1,4-dihydroxybutane in a molar ratio 1 : 1. OH number 56; acid number: 0.9

IV Mixed ester of adipic acid and o-phthalic acid (molar ratio 1 : 1) and 1.6-dihydroxy-hexane, OH number: 62; acid number: 1.5

V Mixed ester of adipic acid and 1,4-dihydroxybutane in a molar ratio, 1,6-dihydroxy-hexane in a molar ratio of 7 : 3. OH number 58; acid number: 0.9

VI Mixed ester, obtained by 8 hours of heating of 1 mol of I and 0.25 mol of II to 190°C. OH number: 62; acid number: 1.2

VII Polyester from o-phthalic acid and ethylene glycol, OH number: 57; acid number: 1.5

VIII Polyester from adipic acid and o-phthalic acid in a molar ratio of 1 : 1 and 1,6-dihydroxy-hexane, OH number: 38.7; acid number: 1.1.

For the preparation of the oligourethanes, the polyesters or polyester mixtures listed in the following Table 1 are dehydrated, together with the optionally employed chain extender (example 3), by 1 hour of heating in a vacuum of 16 mbar at 100°C. The polyisocyanates mentioned in Table 1 are then added during agitation at 100-120°C. After 6 hours of reaction

time at 100-120°C, NCO-group-free conversion products are present, which are then dissolved after cooling at room temperature in ethyl acetate to solutions with a solids content of 50 % by weight. The starting materials of examples 1 to 11, used to produce the oligourethanes, and the viscosities of the resulting solutions are summarized in Table 1.

In order to produce adhesive solutions ready for use, 100 g of the 50 % by weight solutions of the oligourethanes listed in Table 1 are mixed with 10 g of a 75 % by weight solution in ethyl acetate of a reaction product of 3 mol toluene-2,4-diisocyanate with 1 mol trimethylolpropane.

The fresh adhesive solutions so prepared are processed within a period of 60 minutes for the production of film composites. For this purpose, the adhesive solutions are applied with a grooved doctor blade in an amount of about 2 g/m^2, in reference to solids, onto the film surfaces to be joined to each other. The coated films are then heated for a period of 20 seconds to about 80°C. Joining of the films then occurs under the pressure of two rubber rolls. The composite strength (N/15 mm) is determined within 5 minutes after joining in a peeling experiment at a tearing angle of 90° and a tearing rate of 100 mm/min. In order to determine solvent release of the adhesives used to produce the film composites, 5 g of the adhesive solution is weighed into a metal dish with a surface of 54.1 cm^2. The solvent loss is determined at regular time intervals on a plate at 50°C. The numerical values in Table 2 refer to the times (minutes) that elapse to evaporation of 85% of the solvent.

The following film composites were produced:

Composite A: Aluminum (40 µm)
Polyethylene terephthalate (50 µm)

Composite B: Aluminum (40 µm)
Polypropylene (50 µm)

Composite C: Polyamide (50 μm)
Polyethylene (50 μm)

Composite D: Polypropylene (50 μm)
Polyethylene (50 μm)

The determined composite strengths are shown in Table 2. Examples 9 and 11 represent comparative examples (only one incorporated type of dicarboxylic acid).

Table 1

Example	Mol	Polyester	Mol polyester	Mol chain extender	Mol diisocyanate	Viscosity (mPa.s/25°C)
1	1	I	0.25 II	-	0.68 TDI [1]	70
2	1	I	0.25 III	-	0.68 TDI	75
3	1	I	0.25 II	0.6 ethylene glycol	0.93 TDI	85
4	1	IV	0.25 II	-	0.68 TDI	80
5	1	I	0.25 V	-	0.68 TDI	80
6	1	I	0.25 II	-	0.68 H [2]	70
7	1	I	0.25 II	-	0.68 44 [3]	75
8	1	I	-	-	0.55 TDI	75
9	1	II	-	-	0.55 TDI	80
10	1	VI	-	-	0.55 TDI	65
11	1	VII	-	-	0.55 TDI	80
12	1	VIII	0.25 II	-	0.45 TDI	100

1) Mixture of 65 % by weight of toluene-2,4-diisocyanate and 35% by weight of toluene-2,6-diisocyanate

2) Hexane-1,6-diisocyanate

3) Diphenylmethane-4,4'-diisocyanate

Table 2

Example	Ethyl acetate release (min)	Composite A immediately N/15 mm	Composite A after 1 month N/15 mm	Composite B immediately N/15 mm	Composite B after 1 month N/15 mm	Composite C immediately N/15 mm	Composite C after 1 month N/15 mm	Composite D immediately N/15 mm	Composite D after 1 month N/15 mm
1	42	3	Tear	4	7.4	3.8	8.0	4	Tear
2	48	3.4	Tear	4.3	8	3.5	Tear	3.7	Tear
3	50	3.1	9.0	4.5	Tear	4	Tear	3.7	Tear
4	34	2.8	8.5	3.6	9	2.9	11.0	2.8	Tear
5	40	2.9	Tear	3	8.5	3	8.0	3.1	12
6	41	2.8	11.0	3.5	9.3	3.2	9.1	3	Tear
7	53	2.4	Tear	3.4	7.4	3.4	7.4	3.6	Tear
8	150	3.3	Tear	3.3	7.8	3.5	Tear	3.3	Tear
9	35	0.4	Tear	0.3	6	0.5	Tear	0.3	Tear
10	105	3.5	Tear	3.8	9	3.5	9.5	3.2	Tear
11	190	1.5	3.0	2.3	3.5	3.8	3.4	2.3	3.5
12	30	2.9	Tear	3.5	8.0	3.7	8.7	3.8	Tear

Claims

1. Use of solutions with a solids content of at least 45 % by weight in organic solvents, inert relative to isocyanate groups, of

   a) at least one organic polyisocyanate with an (average) NCO functionality of at least 2.0,

   b) at least one oligourethane containing hydroxyl groups with a molecular weight of 1500 to 8000 and

   c) optionally the auxiliaries and additives known from adhesives technology.

   in which the amounts of components a) and b) correspond to an NCO/OH-equivalent ratio of at least 1 : 1.5, as adhesives in the production of foil composites, characterized by the fact that oligourethanes, optionally containing incorporated chain extenders and essentially representing urethane-modified, ether group-free polyester polyols, with a hydroxyl group content from 0.4 to 2.2 % by weight and a urethane group content from 1.4 to 7 % by weight, which contain both aliphatic and aromatic dicarboxylic acid segments, incorporated via ester groups, are used as component b)..

2. Use according to Claim 1, characterized by the fact that reaction products

   b_1) of at least one organic diisocyanate with

   b_2) a polyester mixture, consisting essentially of

   (i) 50 to 90 % by weight of a polyester-diol in the molecular weight range from 1400 to 3000 from adipic acid and o-phthalic acid in a molar ratio of 40 : 60 to 80 : 20 and excess amounts of an alkanediol with 2 to 6 carbon atoms and

(ii) 10 to 50 % by weight of a polyesterdiol in the molecular weight range from 1000 to 3000 from adipic acid and an excess amount of a mixture of at least two different alkanediols with 2 to 6 carbon atoms, in which at least two of the alkanediols are present in an amount of at least 20 mol%,

and optionally

b_3) up to 100 mol%, in reference to component b_2). of at least one di- or trihydric alcohol in the molecular weight range from 62 to 400,

with maintenance of an NCO/OH-equivalent ratio from 1 : 1.2 to 1 : 3, are used as component b) and the components a) and b) are also used in amounts corresponding to an NCO/OH-equivalent ratio from 1 : 1.3 to 1 : 0.5.

3. Use according to Claims 1 and 2, characterized by the fact that a reaction product of

b_1) toluene-2,4-diisocyanate or a mixture of toluene-2,4-diisocyanate with up to 35 % by weight, in reference to the total mixture, of toluene-2,6-diisocyanate with

b_2) a polyester mixture, consisting of 0 to 85 % by weight of a polyester-diol in the molecular weight range 1500 to 2500 from adipic acid and o-phthalic acid in a molar ratio of 40 : 60 to 70 : 30 and ethylene glycol, and 15 to 30 % by weight of a polyester-diol in the molecular weight range from 1500 to 2500 from adipic acid and a mixture of ethylene glycol and 1,4-dihydroxybutane in a molar ratio of 80 : 20 to 20 : 80

is used as component b) while maintaining an NCO/OH-equivalent ratio from 1 : 1.8 to 1 : 3.0.

4. Use according to Claims 1 to 3, characterized by the fact that the adhesives are used as solutions in solvents, inert relative to isocyanate groups, with a solids content from 45 to 70 % by weight.